



Degradation Studies of Cyanex 301

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INTRODUCTION

- CYANEX 301, whose major component is Bis(2,4,4-trimethylpentyl) dithiophosphinic acid, is a well-known commercial extractant.
- The various applications of this extractant have led to many studies on its stability in very different media.
- When CYANEX 301 is contacted with nitric acid, a survey of the literature suggests many different degradation products:
 - ❖ CYANEX 301 has been thought to degrade directly in its oxo-equivalents CYANEX 302 and CYANEX 272.
 - ❖ More recently, a commonly accepted consensus appeared, assessing that the degradation of this molecule follows a two-steps process, the first step consisting in the formation of a dimer made of two molecules of CYANEX 301 linked by a disulfide bridge resulting of the condensation of the -SH groups of the two molecules.

But, as far as we know, no study has ever clearly identified this compound.

This poster presents the identification of this compound which has been made using ³¹P {¹H} NMR analysis.

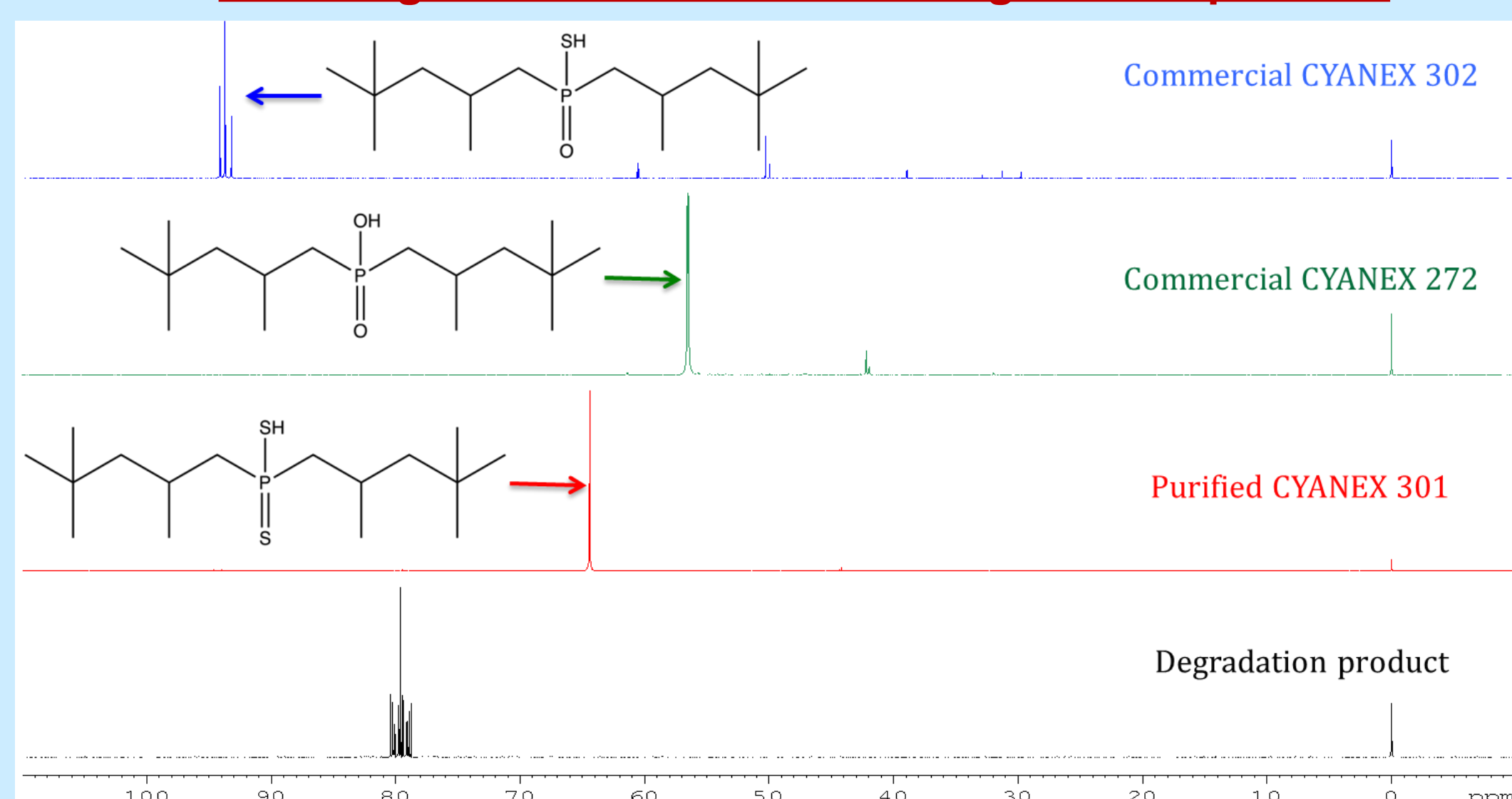
EXPERIMENTAL

- Degradation experiments:
 - ❖ All the sample were stirred at 25°C, using a rotating wheel.
- NMR analysis:
 - ❖ The volume of each sample was 500µl
 - ❖ All the NMR analyses were run with a 0.1M H₃PO₄ in D₂O insert:
 - ✓ The lock was done on D₂O
 - ✓ The signal corresponding to the phosphorous atom of H₃PO₄ was used as a reference and set at δ_p = 0ppm
 - ❖ Two instruments have been used:
 - ✓ The Bruker Avance 400 has been used for most of the analyses
 - ✓ The ³¹P {¹H} homodecoupled NMR analyses required three channels on the amplifier, and have been conducted on a Bruker Avance III 400



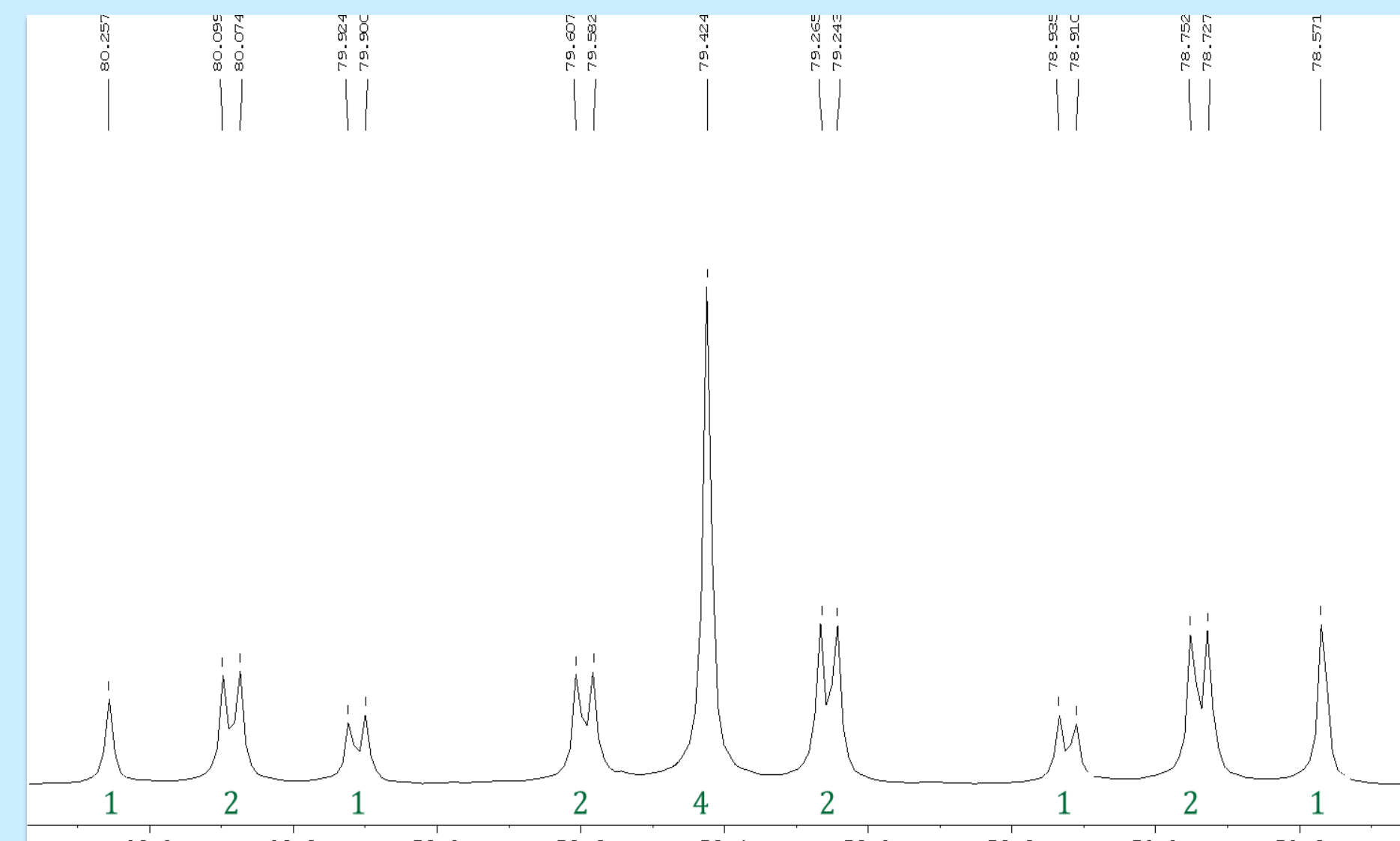
FIRST STUDY OF THE DEGRADATION

- 0.1M CYANEX 301 in toluene has been contacted with 1M HNO₃ for 3 hours. The organic layer was then sampled and analyzed using ³¹P {¹H} NMR.
 - The obtained spectrum has been compared with those of pristine 0.1M CYANEX 301 in toluene, and of 0.1M CYANEX 302 and 272, also prepared in toluene.
- The comparison exhibits a complete degradation of CYANEX 301, but invalidates obtaining CYANEX 302 or 272 as degradation product.**



³¹P NMR ANALYSIS OF THE DEGRADED PRODUCT

- Degraded CYANEX 301 exhibits a complex multiplet at δ_p ≈ 80ppm. An increase of the number of scans (ns = 256) and the lowering of the line broadening value (lb = 0) has led to a clear spectrum of the degraded product.
- Despite the apparent complexity of the spectrum, a symmetry centered on the central peak in the position and integration of the peaks appears. This analysis has also led to identify three peaks as singlets, the other one being doublets.



ISOMERICALLY PURIFIED CYANEX 301: XRD ANALYSIS AND IMPACT ON THE DEGRADATION

- Bis(2,4,4-trimethylpentyl)dithiophosphinic acid possesses two asymmetric carbons, leading to four possible combinations: [R;R], [S;S], [R;S] and [S;R]. The four isomers are present in equal proportions in the primary mixture.
- An isomeric purification of this primary mixture has led to the first crystallized CYANEX 301 ammonium salt:
 - ❖ The crystal was found to belong to the monoclinic C2/c space group.
 - ❖ The crystal contains a 50:50 mixture of the RR and SS enantiomers. Anions of the same chirality (RR or SS) form N-H...S hydrogen-bonds with the ammonium cations, resulting in two-dimensional layers in the crystallographic ab plane (Figure 1).
 - ❖ Finally, layers of opposite chirality alternate along the crystallographic c axis, packing via van der Waals interactions (Figure 2).

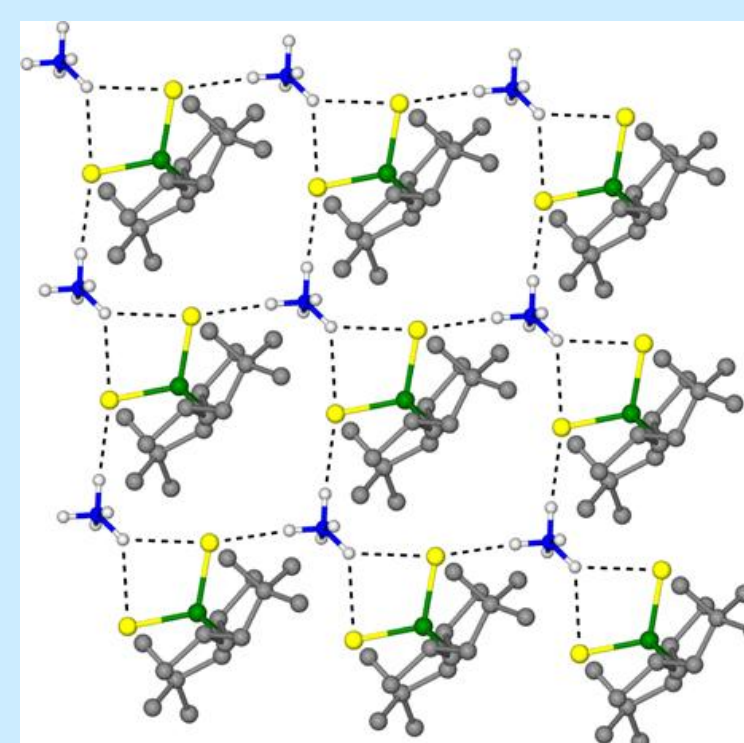


Figure 1

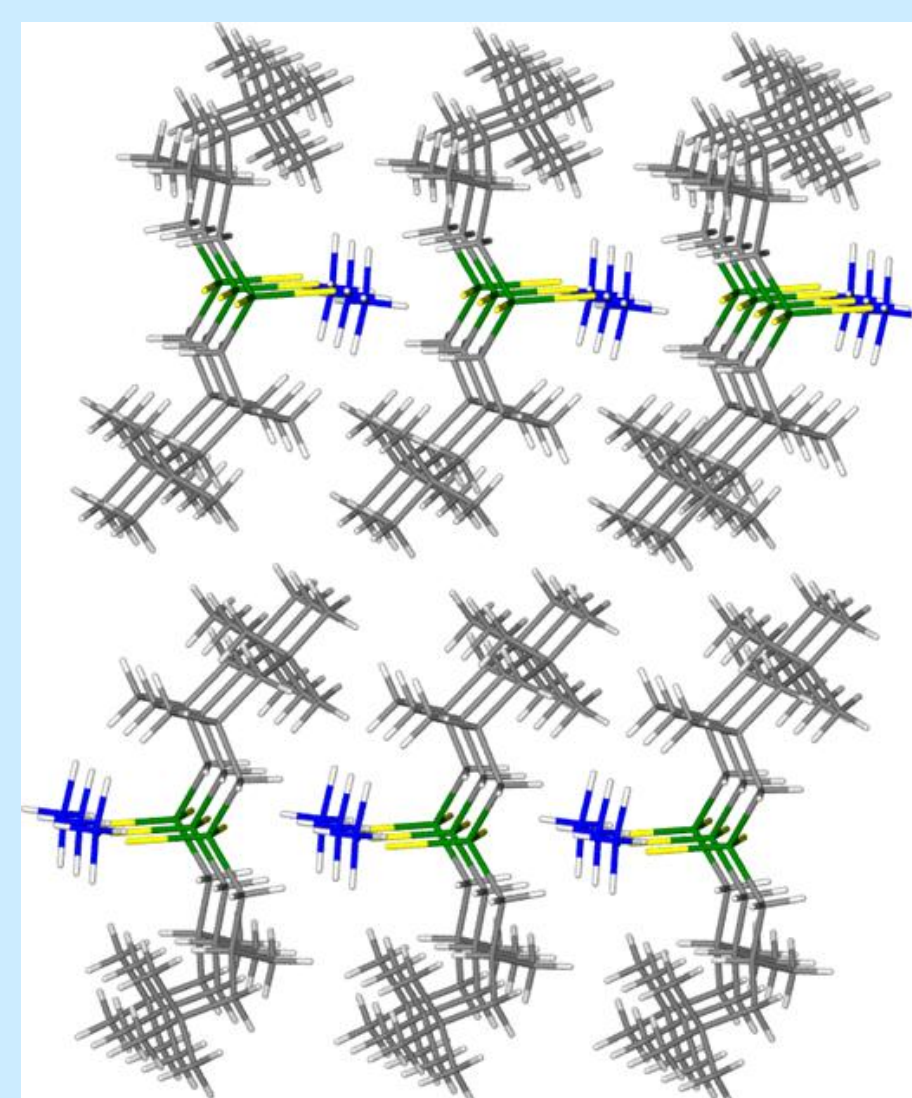
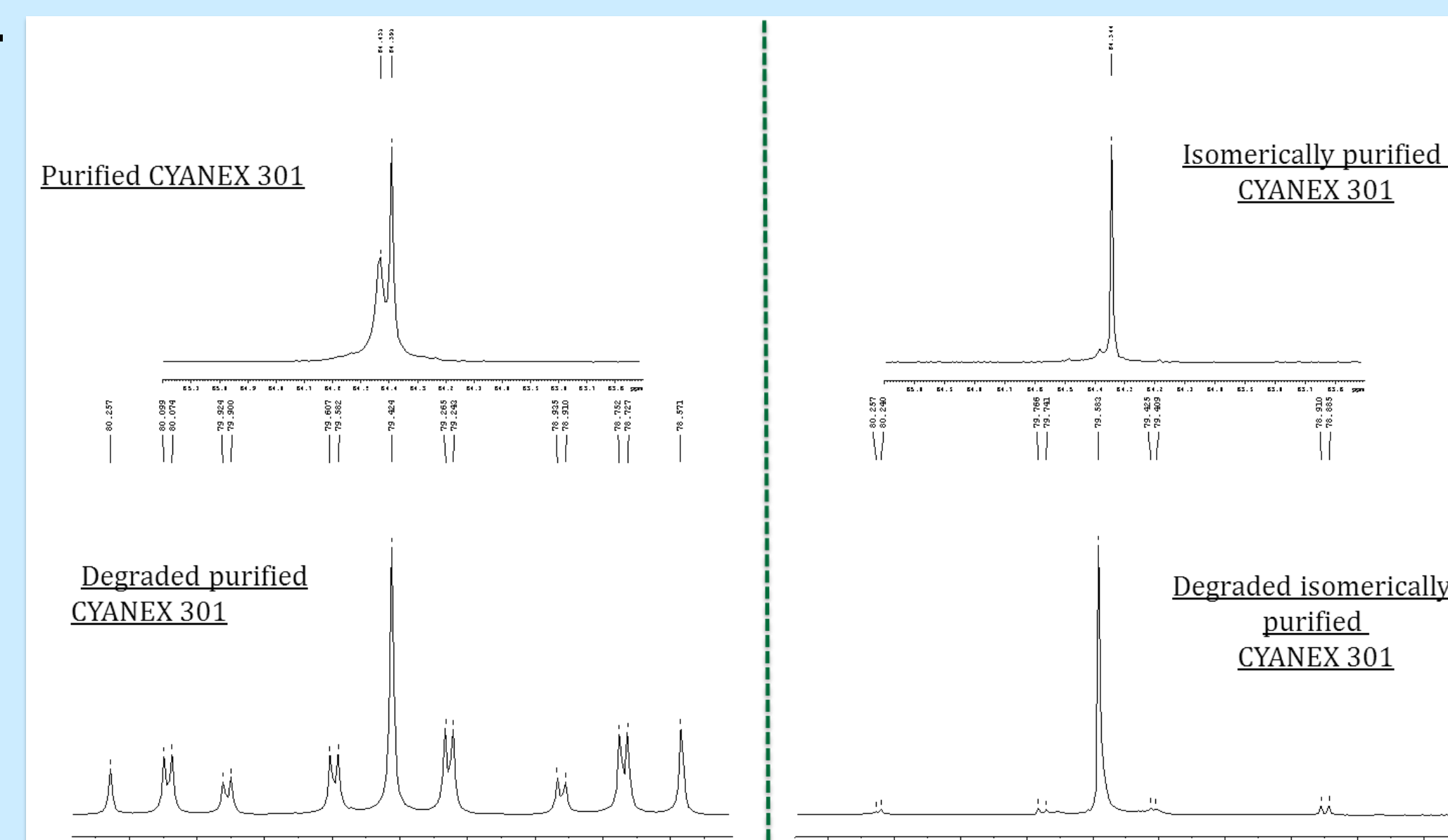


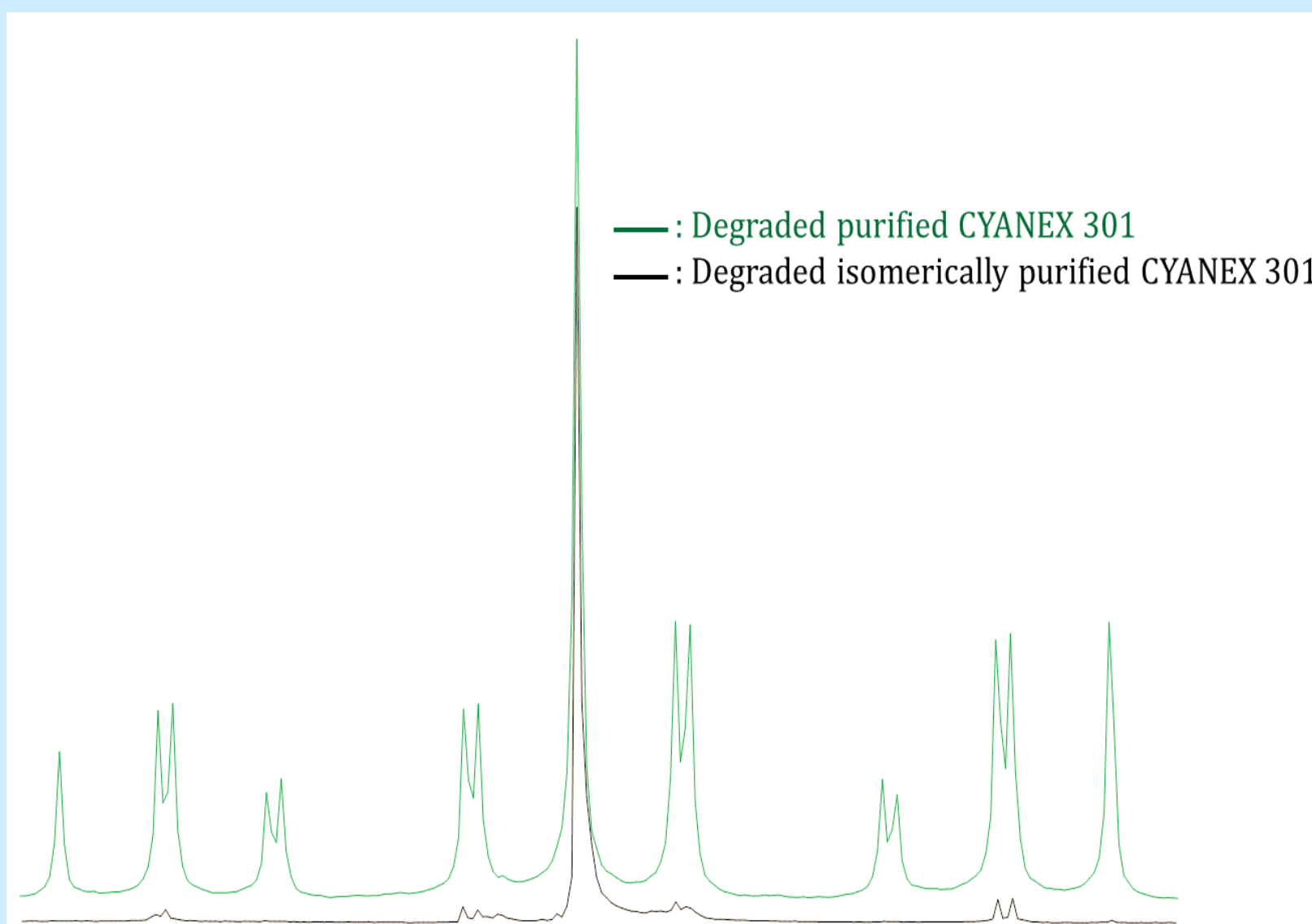
Figure 2

- The isomeric purification has a clear impact on the ³¹P {¹H} NMR spectrum of CYANEX 301. It appears that each of the two peaks obtained for the racemic mixture corresponds to a couple of enantiomers.
- The isomeric purification results also in a huge difference on the spectrum of the degraded product.



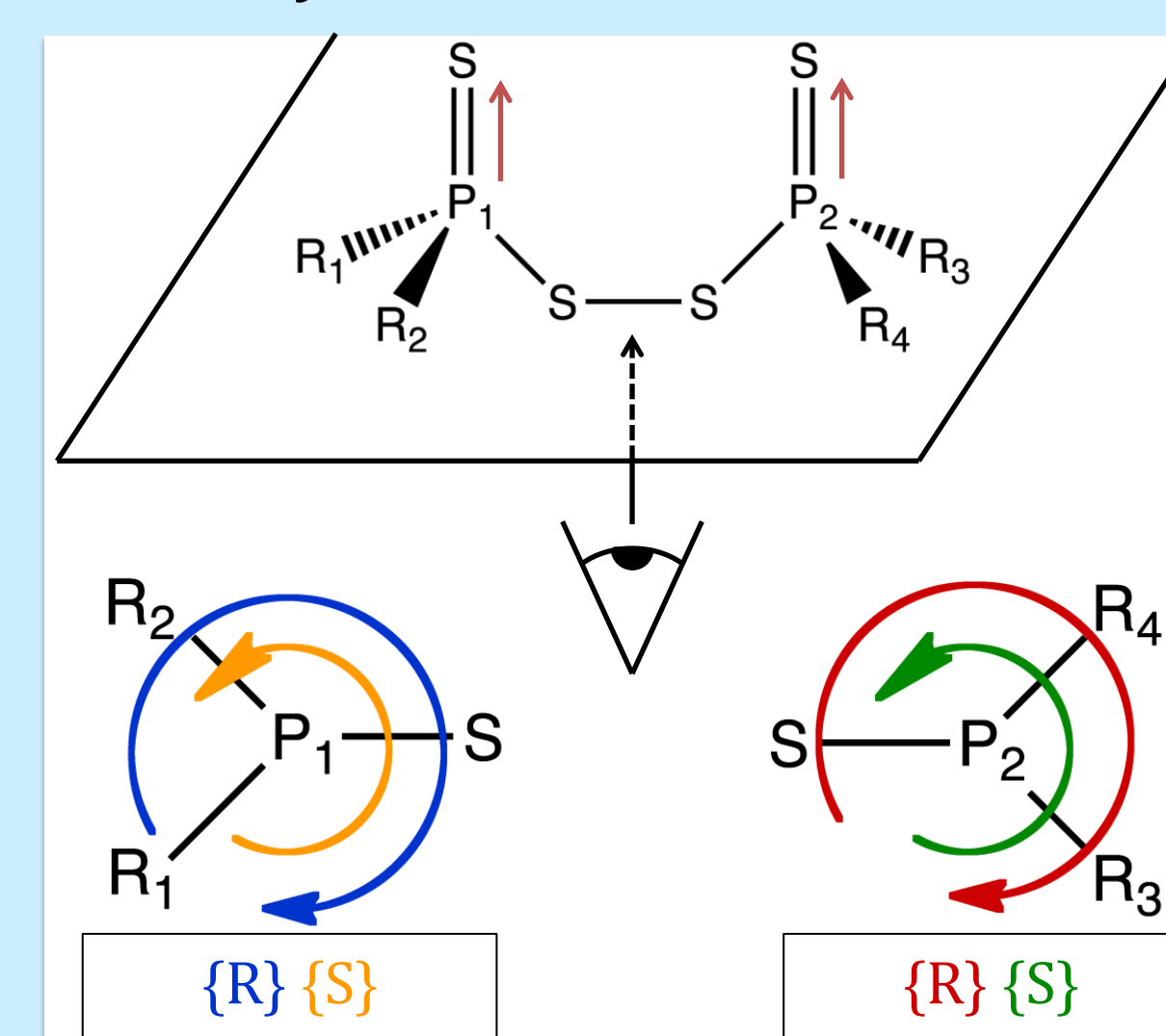
COMPARISON OF THE SPECTRA

- The superimposition of the two spectra clearly shows that the removal of [R;S] and [S;R] isomers has led to a spectrum where only the central peak remains, with small traces of other peaks (probably due to traces of [R;S] and [S;R] isomers still present).
- This comparison shows that the multiplet obtained for degraded purified CYANEX 301 has for origin the different combinations of asymmetric carbons on the alkyl chains. It was also noted that phosphorous atoms may exhibit asymmetric character.**



ASYMMETRY OF THE PHOSPHOROUS ATOMS

- Depending on the nature of the asymmetric carbons of the linked alkyl chains, the phosphorous atoms can exhibit three different asymmetric characters:
 - ❖ Non-Asymmetric {NAs} when the two asymmetric carbons have the same descriptor ([R;R] or [S;S])
 - ❖ {R} or {S}, defined by using an adapted version of the Cahn, Ingold and Prelog rules:
 - ✓ P=S defines the axis and direction
 - ✓ P-S has the priority on alkyl chains
 - ✓ An [R] chain has the priority on an [S]



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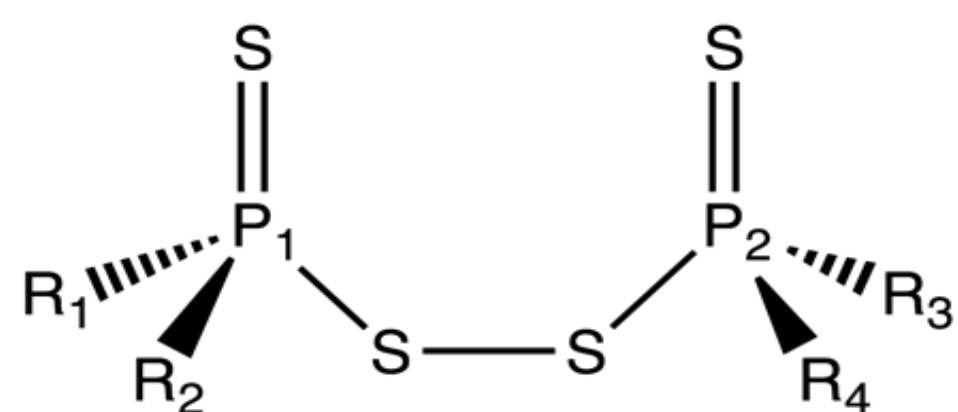
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PHOSPHOROUS ASYMMETRY IN THE DISULFIDE

- Given these rules, all the possible combinations of asymmetric carbons, and their impact on the asymmetry of the phosphorous atoms, have been determined, leading to 16 different possibilities, presented in the table below.

Phosphorus 1	Phosphorus 2	P Asymmetry	Allocation
[R;R]	[R;R]	{NAS;NAS}	{P ₁ ;P ₂ }
[R;R]	[S;S]	{NAS;NAS}	Phosphorus 1 [R ₁ ;R ₂]
[R;R]	[R;S]	{NAS;S}	Phosphorus 2 [R ₃ ;R ₄]
[R;R]	[S;R]	{NAS;R}	
[S;S]	[R;R]	{NAS;NAS}	
[S;S]	[S;S]	{NAS;NAS}	
[S;S]	[R;S]	{NAS;S}	
[S;S]	[S;R]	{NAS;R}	
[R;S]	[R;R]	{R;NAS}	
[R;S]	[S;S]	{R;NAS}	
[R;S]	[R;S]	{R;S}	
[R;S]	[S;R]	{R;R}	
[S;R]	[R;R]	{S;NAS}	
[S;R]	[S;S]	{S;NAS}	
[S;R]	[R;S]	{S;R}	
[S;R]	[S;R]	{S;S}	



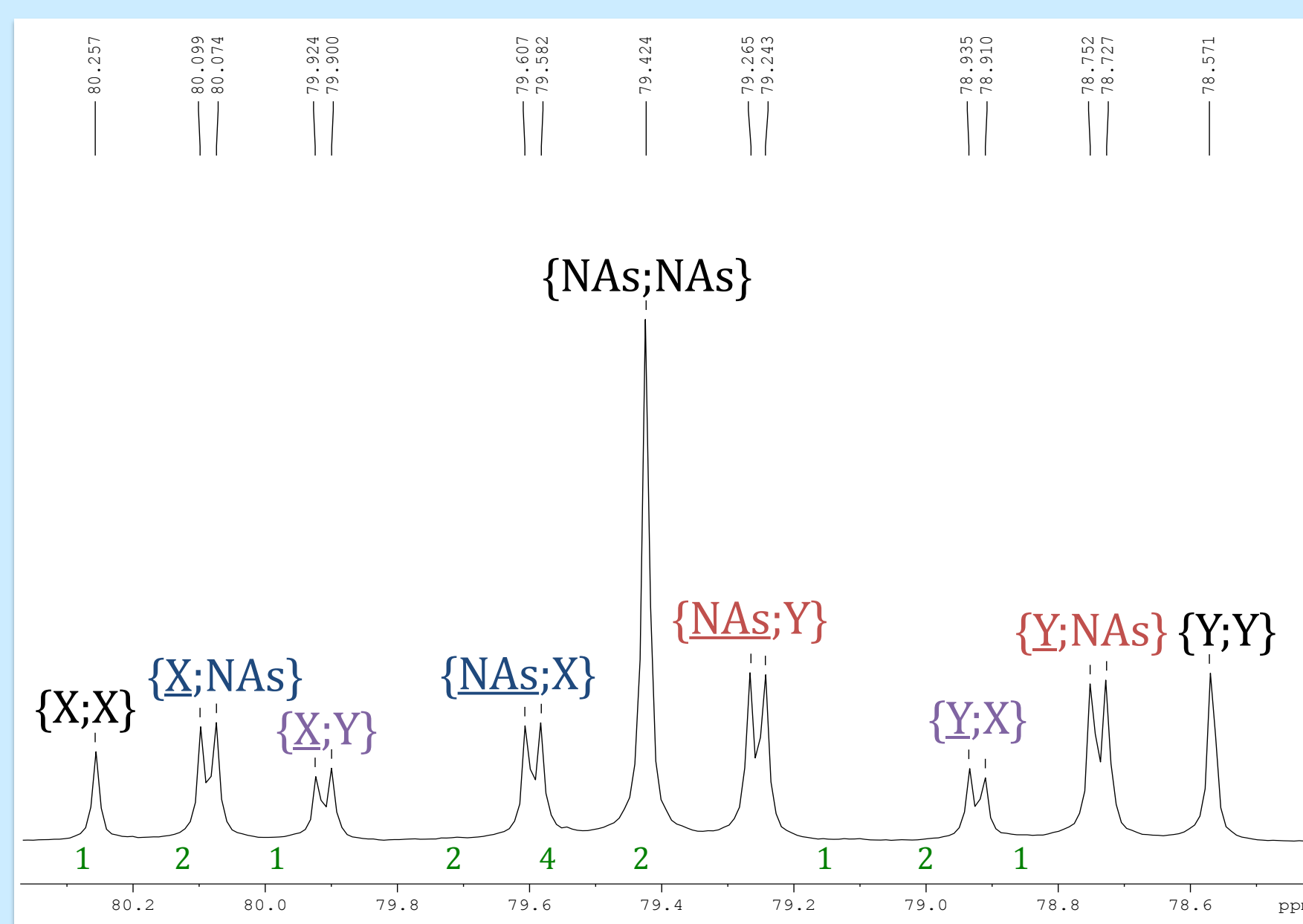
- These results have then been refined taking in account the symmetry of the disulfide, and grouped by phosphorous asymmetry. For each case, a probability of formation of the corresponding compound is given considering a racemic mixture of the four isomers of CYANEX 301, and an equiprobability of association of the different isomers when condensing to yield to the disulfide.

Case	Comments	Probability of formation
{NAS;NAS}	Made of two enantiomers {[S;S];[S;S]} and {[R;R];[R;R]} and their diastereoisomers, which are in fact one molecule {[R;R];[S;S]} (a rotation gives {[S;S];[R;R]}) . Possibility to distinguish the diastereoisomers in NMR in some cases.	4
{NAS;R} and {R;NAS}	Made of only two enantiomers {[R;S];[RR]} and {[R;S];[S;S]}, these two possibilities are equivalent (considering one enantiomer, a rotation can change [NAS;R] in [R;NAS], and reversly).	4
{NAS;S} and {S;NAS}	Made of only two enantiomers {[S;R];[RR]} and {[S;R];[S;S]}, these two possibilities are equivalent (considering one enantiomer, a rotation can change [NAS;S] in [S;NAS], and reversly).	4
{R;R} and {S;S}	Each of these two possibilities is made with only one molecule (it is impossible to distinguish the two phosphorus when they have the same stereo-descriptor). [R;R] and [S;S] are "double" diastereoisomers : considering alkyl chains, and phosphorus.	1 Each
{R;S} and {S;R}	These two possibilities are in fact only one molecule. The couples {[R;S];[R;S]} and {[S;R];[S;R]} are equivalent.	2

ATTRIBUTION OF THE PEAKS

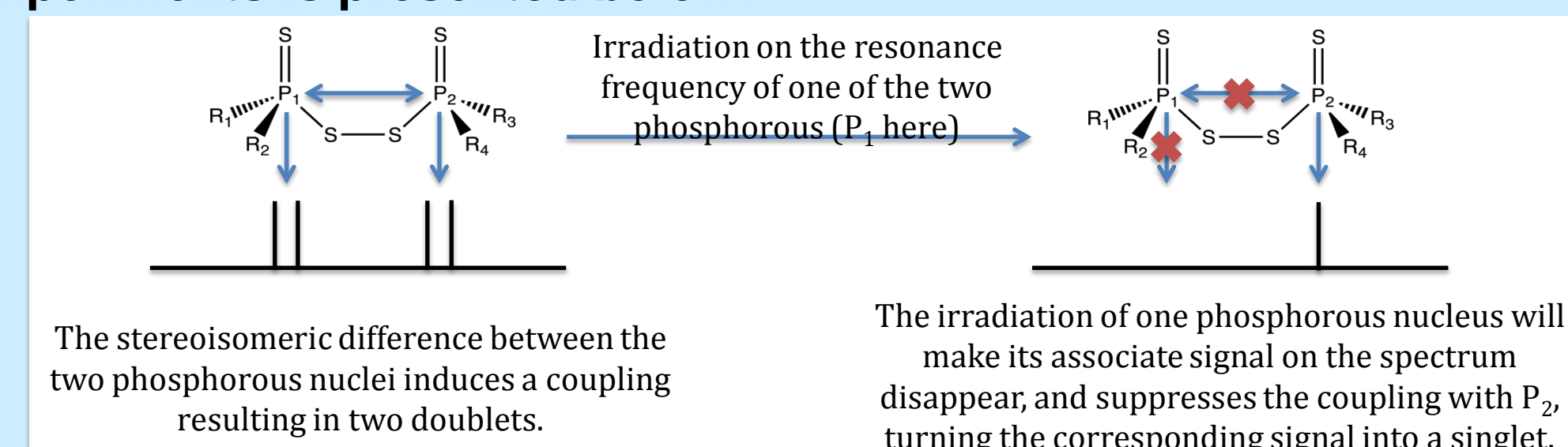
- It has not been possible to ascribe a side for the {R} and {S} phosphorous atoms. That's why they are designated with the letters {X} and {Y}.
- The attribution has been done considering that:

- ❖ Coupling occurs only between two stereoisomerically different phosphorous atoms
- ❖ Considering the mixture as racemic, the integration of the peaks must fit the formation probability
- ❖ Considering a given (R,S or NAs) phosphorous atom, the impact on its chemical shift when bridged to a stereoisomerically different phosphorous is all the more important as the difference of the chemical shifts of the associated singlets is important.

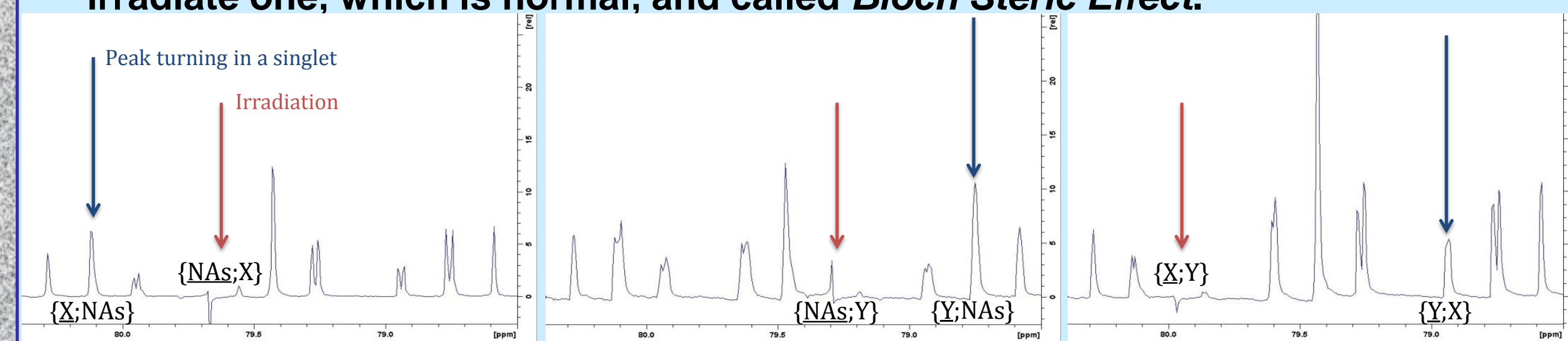


VALIDATION OF THE COUPLING

- To validate that the origin of the doubled peaks is a coupling between two phosphorous atoms, we have run ³¹P {¹H} homodecoupled NMR. The principle of these experiments is presented below:



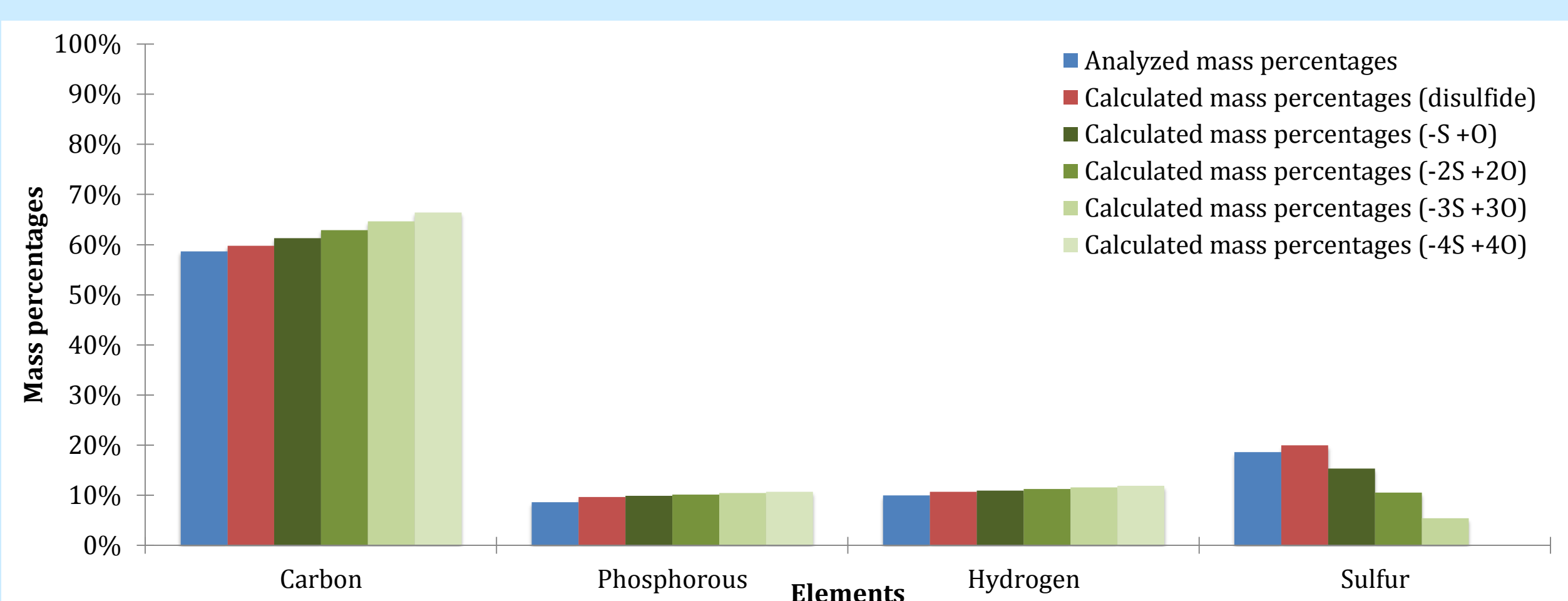
- It is possible to observe a loss of multiplicity on the peaks directly around the irradiate one, which is normal, and called *Bloch Steric Effect*.



ELEMENTAL ANALYSIS

- Degraded CYANEX 301 was sent to Galbraith Laboratories for elemental analysis.
- Oxygen was not analyzed due to the presence of phosphorous atoms in the compound.
- Mass percentages were calculated for the disulfide, and also for all the possible oxo-equivalents of the disulfide.

Results match the disulfide formation



PROPOSED REACTION EQUATION

- **Role of the acid and oxidizer:**

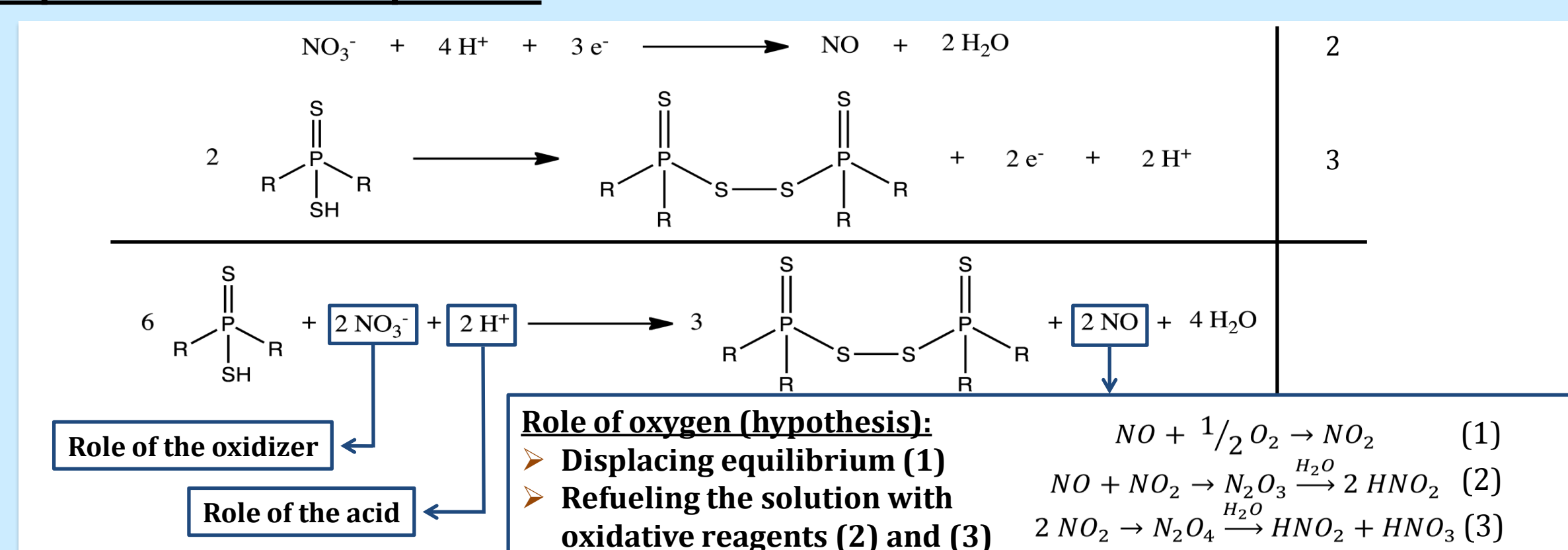
CYANEX 301 contacted with	Time contacted	30 minutes	3 hours
1M HCl	-	-	ND
1M HNO ₃	PD	PD	CD
1M HNO ₃ + 10mM NaNO ₂	CD	CD	-
1M NaNO ₃ + 10mM NaNO ₂	-	-	ND

- **Impact of the atmosphere:**

Atmosphere	Analysis after 3 hours
Open to air	CD
Sealed under air	CD
Sealed under Ar	ND

ND : No Degradation
PD : Partial Degradation
CD : Complete Degradation

- **Proposed reaction equation:**



FIRST SURVEY ON THE IMPACT OF SUBSTITUENTS

- 10mM of each compound prepared freshly have been used for the degradation with 1M HNO₃ + 0.1mM NaNO₂

Compound	Time contacted	1M HNO ₃ + 0.1 mM NaNO ₂	Compound	Time contacted	1M HNO ₃ + 0.1 mM NaNO ₂
	30 minutes	PD or ND		30 minutes	PD (66%)
	1 hour	CD		1 hour	CD
	2 hours	-		2 hours	-
	4 hours	-		4 hours	-
	8 hours	-		8 hours	-
	24 hours	-		24 hours	-
	30 minutes	ND		30 minutes	PD (33%)
	1 hour	PD (50%)		1 hour	CD
	2 hours	CD		2 hours	-
	4 hours	-		4 hours	-
	8 hours	-		8 hours	-
	24 hours	-		24 hours	-
	30 minutes	ND		30 minutes	ND
	1 hour	ND		1 hour	PD (very light)
	2 hours	ND		2 hours	CD
	4 hours	ND		4 hours	-
	8 hours	ND		8 hours	-
	24 hours	ND		24 hours	-
	30 minutes	ND		30 minutes	ND
	1 hour	ND		1 hour	PD (50%)
	2 hours	ND		2 hours	CD
	4 hours	ND		4 hours	-
	8 hours	ND		8 hours	-
	24 hours	ND		24 hours	-
	30 minutes	ND		30 minutes	ND
	1 hour	ND		1 hour	ND
	2 hours	ND		2 hours	CD
	4 hours	ND		4 hours	-
	8 hours	ND		8 hours	-
	24 hours	ND		24 hours	-

ND No Degradation
PD (X%) Partial Degradation (estimation "with the eyes" of the degraded amount)
CD Complete Degradation

CONCLUSION

- **Identification of the degradation product:**
- ❖ First time ³¹P NMR analysis was used to study the degradation of CYANEX 301.
 - ❖ The hypothesis of the formation of a dimer of two molecules of CYANEX 301 linked by a disulfide bridge has been validated by the identification of the degradation product using elemental analysis.
 - ❖ The ³¹P {¹H} NMR spectrum has been thoroughly explained, the last point to figure out being the exact attribution of {R} and {S} phosphorous nuclei.
- **Impact of some parameters on the degradation:**
- ❖ Demonstrated need of both an acid and oxidizer for the degradation to take place.
 - ❖ Identification of a role of the atmosphere, probably of oxygen, in the degradation process.
- **First survey of the stability of some other substituted dithiophosphinic acids:**
- ❖ Identification of two compounds remaining intact after 24 hours of contact.

ACKNOWLEDGMENTS

We are thankful to Mike Brown from Bruker for writing the pulse program, and for his precious help for the homodecoupling NMR experiments.
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